Supporting Information

Cobalt-catalyzed Synthesis of *N*-containing Heterocycles via Cyclization of Ortho-substituted Anilines with CO_2/H_2

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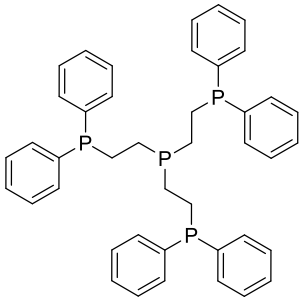
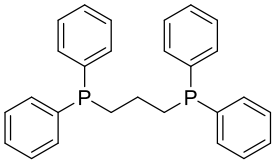
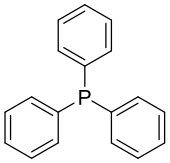
Effects of ligands on the cyclization reaction

Table S1 Effects of ligands on the cyclization reaction [a]

Entry	Ligand	Yield (%)
1		2
2		<1
3		3

Reaction conditions: [a] *o*-phenylenediamine (1.0 mmol), CoF_2 (10 mol %), ligand (5 mmol %), CsF (1.5 equiv.), EtOH (3 mL), CO_2 pressure of 3 MPa, total pressure of 6 MPa, 140 °C, 24 h. The yield was determined by ^1H NMR, calibrated using 1,1,2,2-tetrachloroethane as the internal standard.

CsF activates ortho-substituted anilines via hydrogen bond interaction

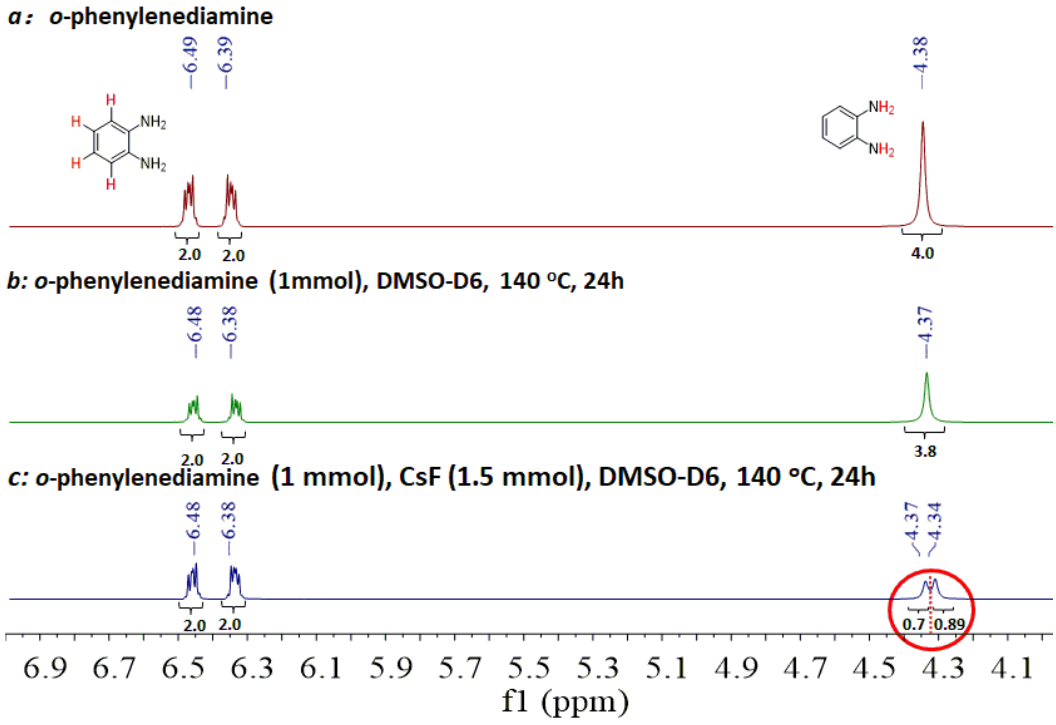


Figure S1. ^{1}H NMR spectra: a) *o*-phenylenediamine; b) *o*-phenylenediamine (1.0 mmol), DMSO-d_6 (2.0 mL), 140 °C, 24h; c) *o*-phenylenediamine (1.0 mmol), CsF (1.5 equiv.), DMSO-d_6 (2.0 mL), 140 °C, 24h.

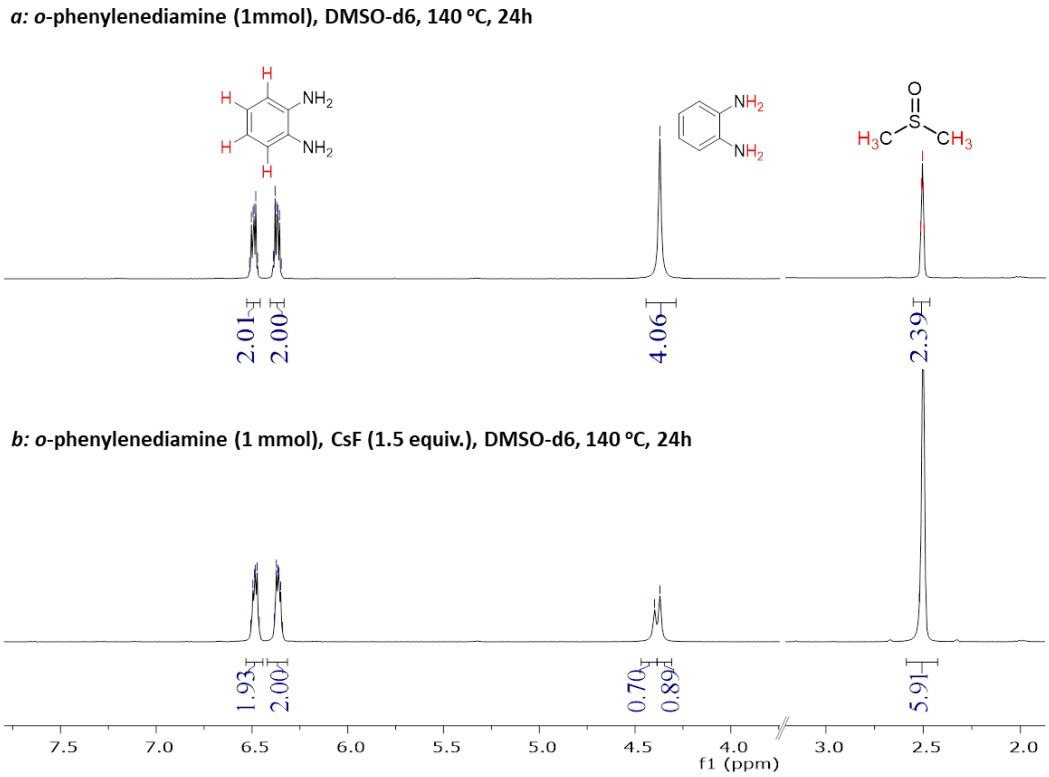


Figure S2 ^{1}H NMR spectra: a) *o*-phenylenediamine (1.0 mmol), DMSO-d6 (2.0 mL), 140 °C, 24h; b) *o*-phenylenediamine (1.0 mmol), CsF (1.5 equiv), DMSO-d6 (2.0 mL), 140 °C, 24h.

Analysis: Counting the H number of in *o*-phenylenediamine from the above ^{1}H NMR spectra ***a*** and ***b*** (Figure S2), it was found that the H number of -NH_2 in *o*-phenylenediamine was decreasing from 4.06 to 1.59 (relative to the hydrogen atoms of benzene ring), while the H number of C-H in DMSO increased form 2.39 to 5.91 (the H number of DMSO was calibrated using the aromatic hydrogen of *o*-phenylenediamine as internal standard). At the same time, the –ND_2 (4.38 ppm) was observed in the ^{2}H NMR spectrum of the mixture of *o*-phenylenediamine and CsF (Figure S3). It is the evidence of H/D exchange between the –NH_2 of *o*-phenylenediamine with –CD_3 of DMSO-d6 in the presence of CsF. It suggests that CsF can activate –NH_2 of *o*-phenylenediamine.

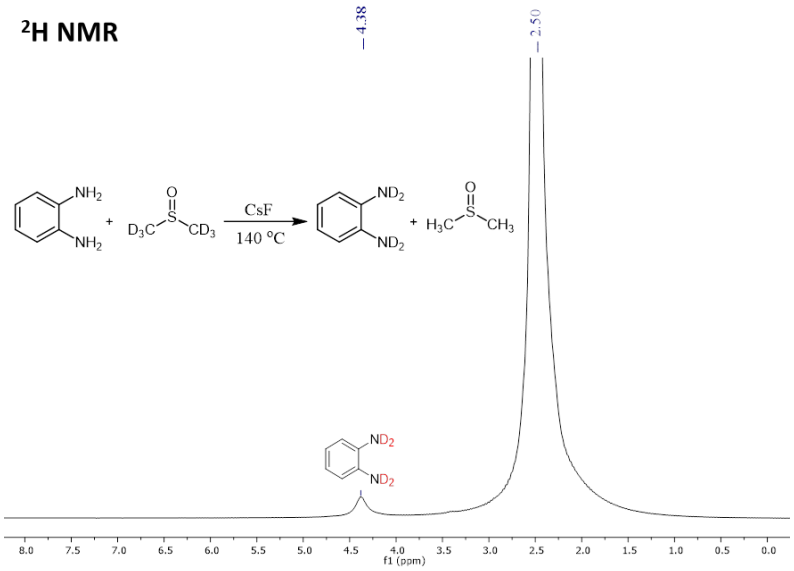


Figure S3 ^{2}H NMR spectrum of the mixture: *o*-phenylenediamine (1.0 mmol), CsF (1.5 equiv), DMSO-d6 (2.0 mL), 140 °C, 24h.

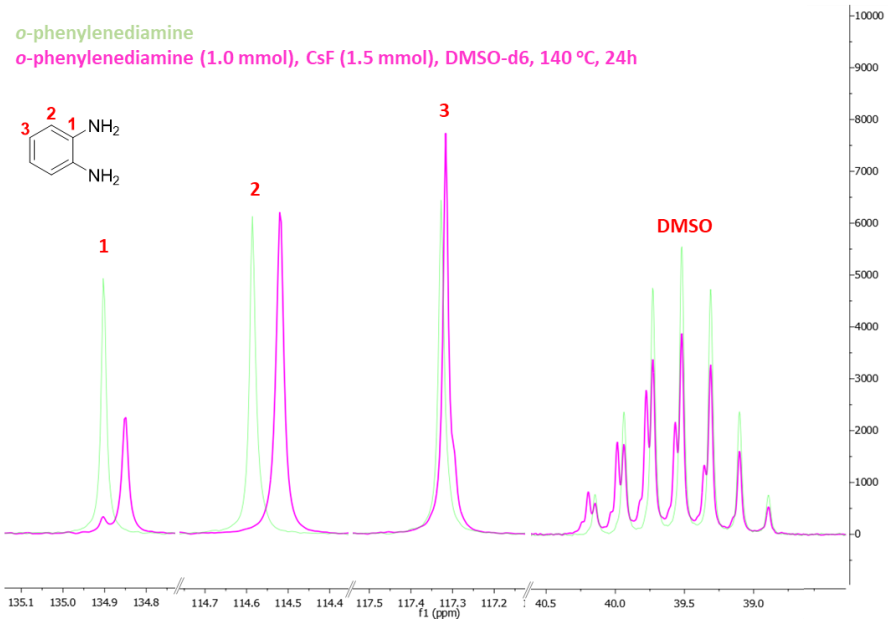


Figure S4 ^{13}C NMR spectra of the mixture: *o*-phenylenediamine (1.0 mmol), DMSO-d6 (2.0 mL), 140 °C, 24h, (Green line); *o*-phenylenediamine (1.0 mmol) with CsF (1.5 equiv) in DMSO-d6 (2.0 mL), 140 °C, 24h (Red line).

Analysis: Comparing the ^{13}C signals of the mixtures of *o*-phenylenediamine, DMSO-d_6 with or without CsF (Figure S4), it was found that the chemical shift of *o*-phenylenediamine shifted upfield from 134.90 (C1), 117.33 (C2), 114.59 ppm (C3) to 134.85 (C1), 117.32 (C2), 114.52 ppm (C3). Carbon atoms of *o*-phenylenediamine become more electron-rich when mixed with CsF, suggesting that the carbon atom of *o*-phenylenediamine was activated by CsF to some extent.

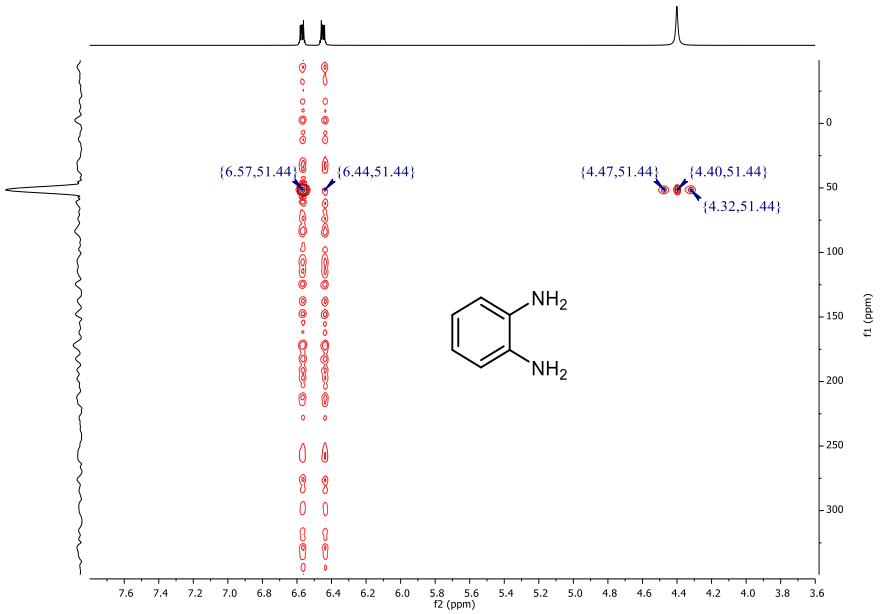


Figure S5 ^{1}H-^{15}N HMBC spectrum of *o*-phenylenediamine (DMSO-d_6, 500 MHz) recorded with an evolution delay τ of 62.5 ms for the optimal detection of long-range J_{H-N} of 8 Hz. ^{15}N NMR (51 MHz, DMSO): δ 51.44, 51.44, 51.44, 51.44, 51.44. ^{1}H NMR (500 MHz, DMSO): δ 6.57, 6.44, 4.47, 4.40, 4.32.

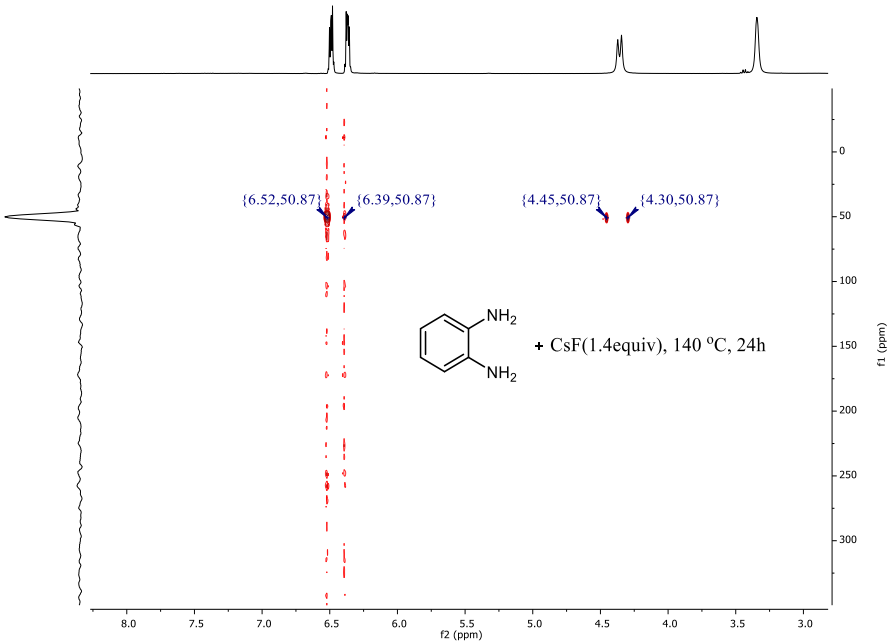


Figure S6 ^{1}H-^{15}N HMBC spectrum of the mixture: *o*-phenylenediamine (1.0 mmol), CsF (1.5 equiv), DMSO-d_6 (2.0 mL), 140 °C, 24h (DMSO-d_6, 500 MHz) recorded with an evolution delay τ of 62.5 ms for the optimal detection of long-range J_{H-N} of 8 Hz.^{15}N NMR (51 MHz, DMSO): δ 50.87, 50.87, 50.87, 50.87. ^{1}H NMR (500 MHz, DMSO): δ 6.52, 6.39, 4.45, 4.30.

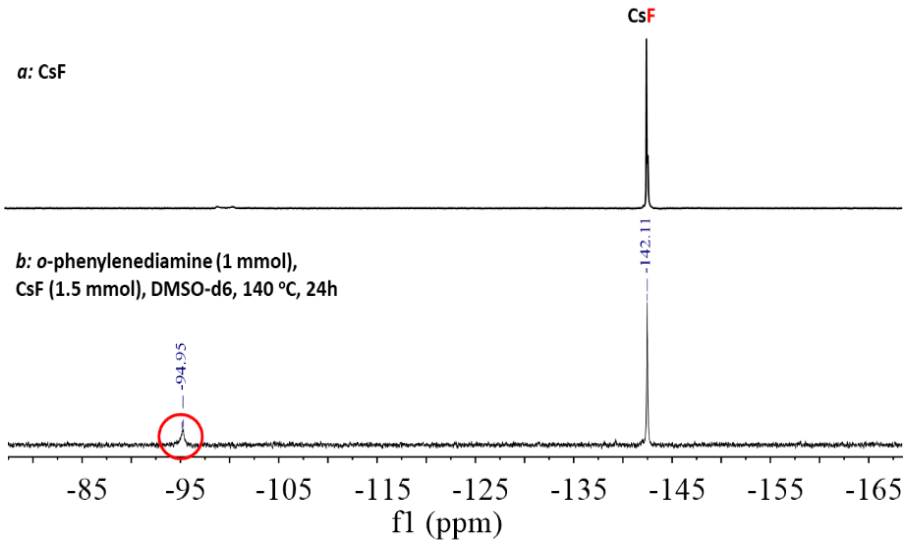


Figure S7. ^{19}F NMR spectra: a) CsF; b) **1a** (1.0 mmol), CsF (1.5 equiv.), DMSO-d_6 (2.0 mL), 140 °C, 24h.

Control experiments

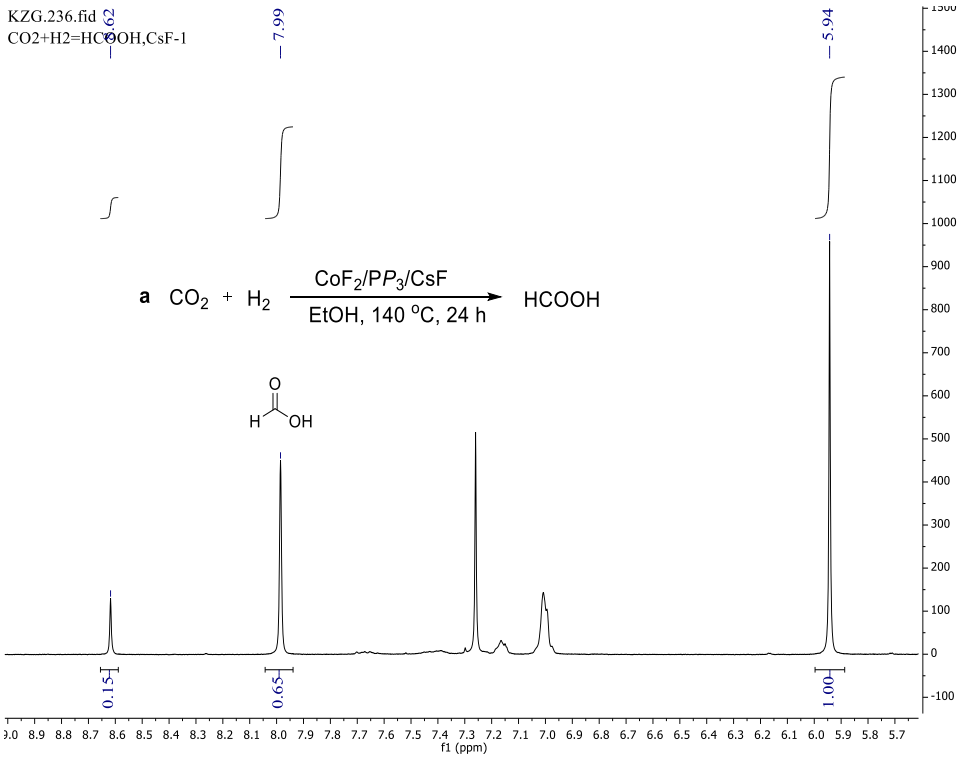


Figure S8 ^{1}H NMR spectrum of the products of Scheme 2a. The yield was determined by ^{1}H NMR, calibrated using 1,1,2,2-tetrachloroethane as the internal standard.

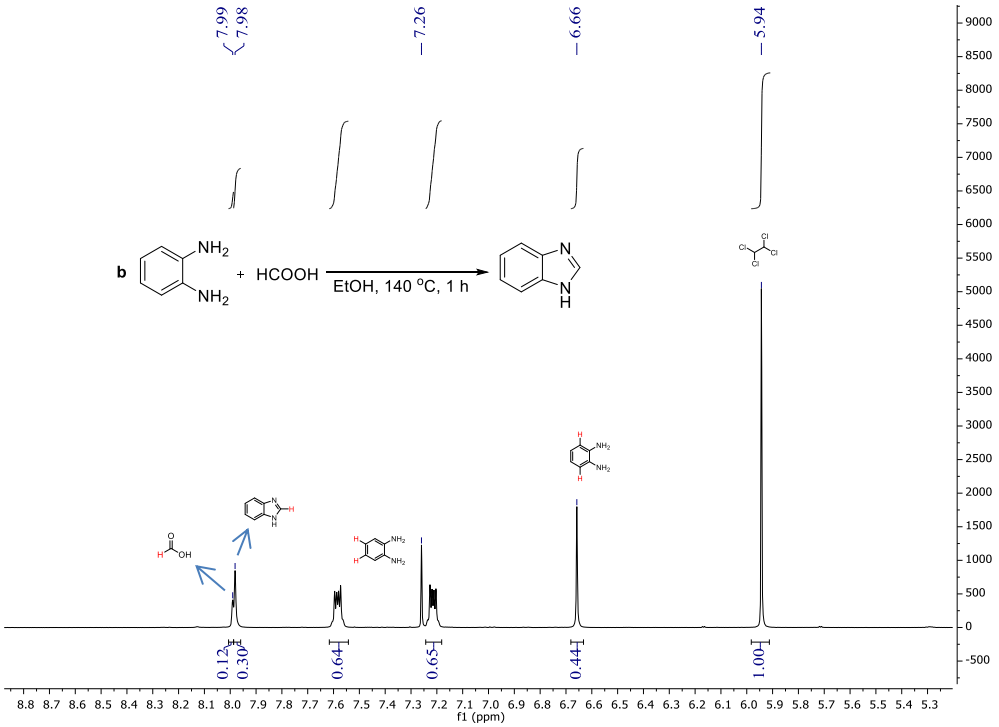


Figure S9 ^{1}H NMR spectrum of the products of Scheme 2b. The yield was determined by ^{1}H NMR, calibrated using 1,1,2,2-tetrachloroethane as the internal standard.

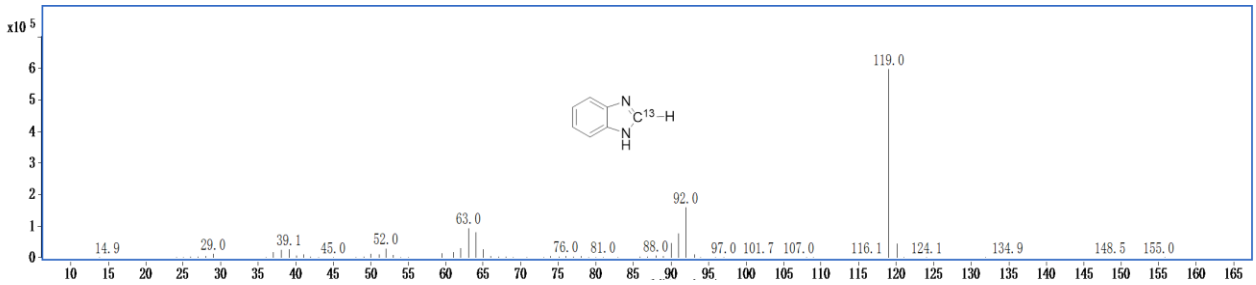


Figure S10 MS spectrum of the cyclization reaction product in the $^{13}CO_2$ isotope labelling experiment, Scheme 2c.

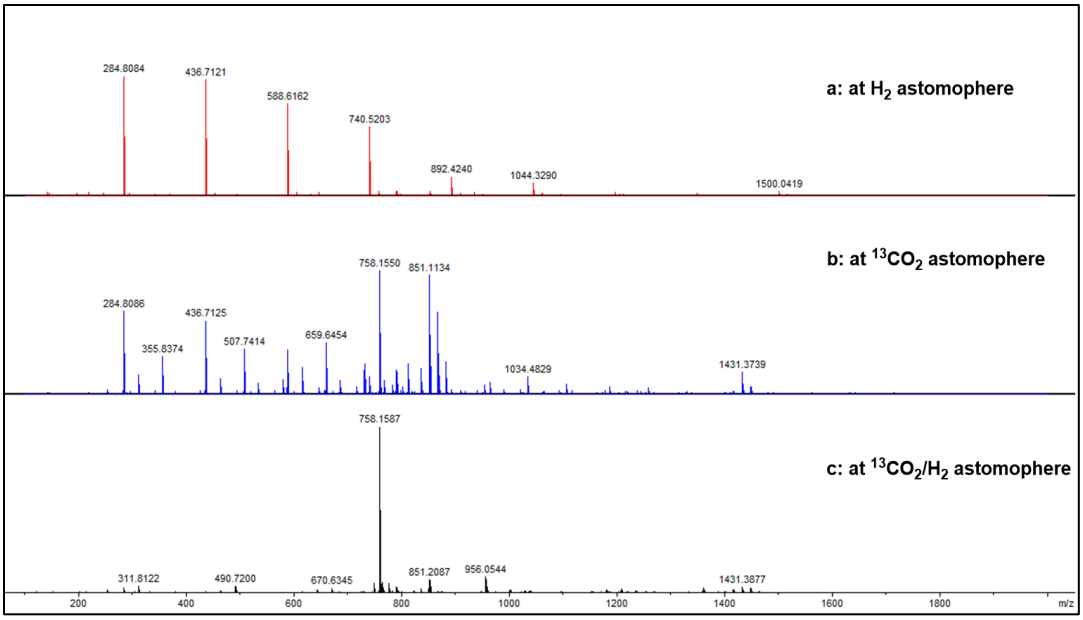


Figure S11 ESI-MS spectra of the reaction mixture at different atmosphere. a, H_2 (3 MPa); b, $^{13}CO_2$ (0.8 MPa); c, $^{13}CO_2$ (0.8 MPa) and H_2 (3 MPa). Reaction conditions: CoF_2 (0.1 mmol), P*P*$_3$ (0.05 mmol), CsF (1.5 mmol), *o*-phenylenediamine (1.0 mmol), EtOH-D_6 (2 mL), 140 °C, 1.5h.

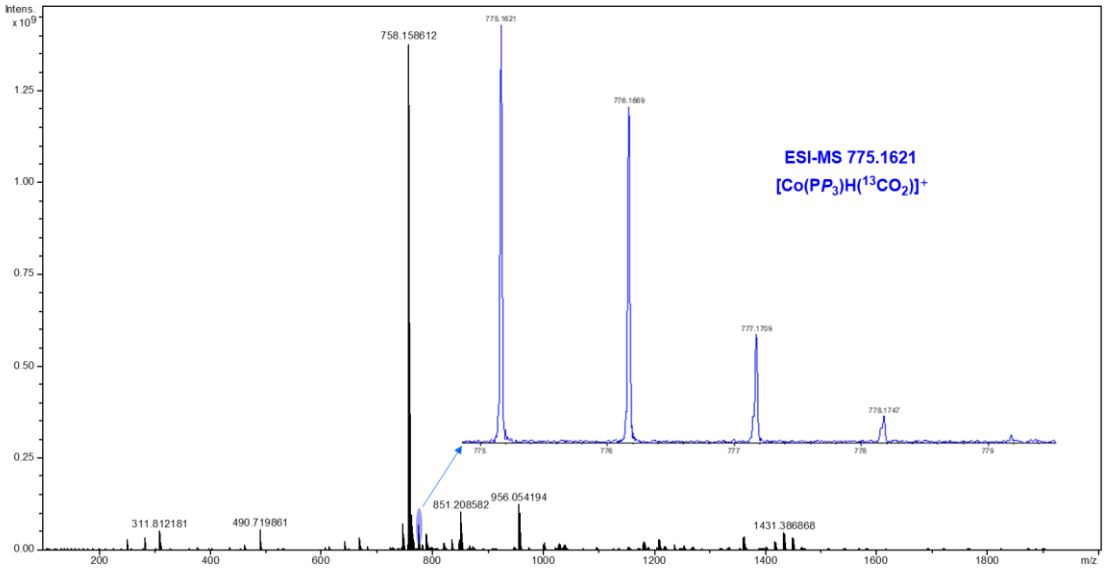


Figure S12 HR-ESI-MS spectrum of the mixture of **1a** (1.0 mmol), CoF_2 (0.1 mmol), P*P*$_3$ (0.05 mmol), CsF (1.5 mmol), EtOH-D_6 (1.0 mL), $^{13}CO_2$ (0.8 MPa), H_2 (3.0 MPa), 140 °C, 1.5 h.

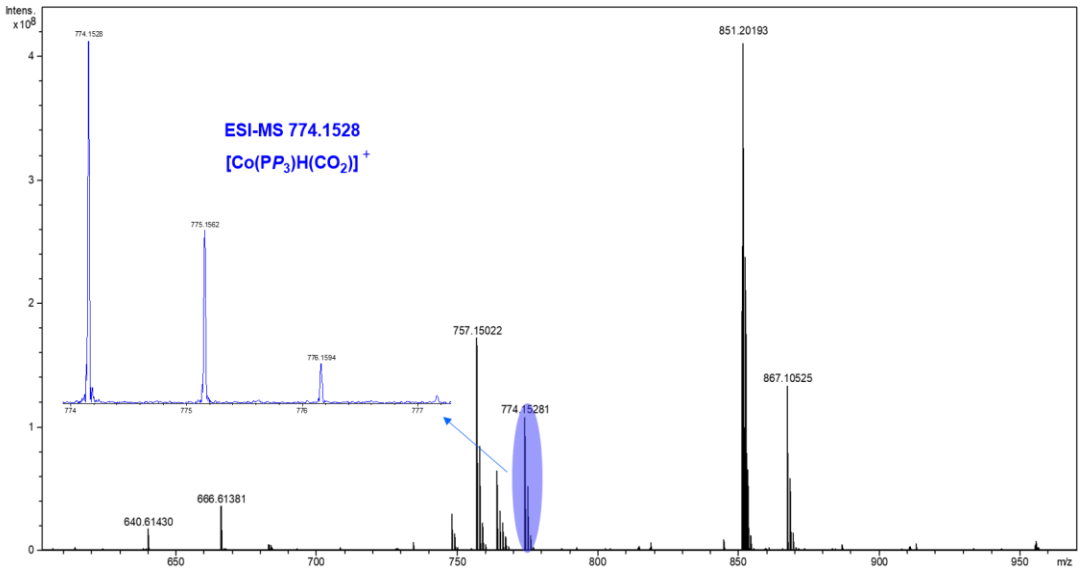


Figure S13 ESI-MS spectrum of the mixture of **1a** (1.0 mmol), CoF_2 (0.1 mmol), P*P*$_3$ (0.05 mmol), CsF (1.5 mmol), EtOH (2.0 mL), CO_2 (3 MPa), H_2 (3.0 MPa), 140 °C, 1.5 h.

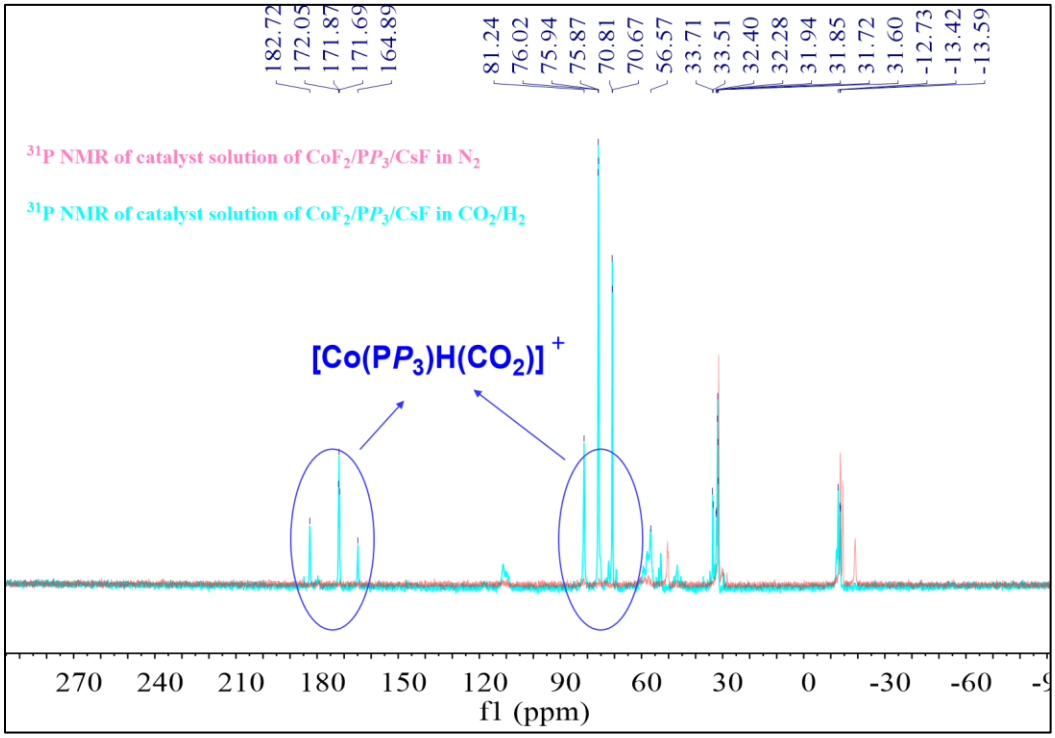


Figure S14 ^{31}P NMR spectra of the catalyst solvent of **1a** (1.0 mmol), CoF_2 (0.1 mmol), P*P*$_3$ (0.05 mmol), CsF (1.5 mmol), EtOH-d_6 (2.0 mL), at different atmosphere, 140 °C, 1.5 h.

^{1}H and ^{13}C NMR and HR-MS (ESI) data of isolated *N*-containing heterocycles

Benzimidazole (**1b**): White solid, yield=94%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.76-7.60 (m, 2H), 7.31 (m, 2H), 6.59 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.53, 137.73, 123.14, 115.70, 77.48, 77.16, 76.84.

6-methyl-1H-benzo[d]imidazole (**2b**): White solid, yield=93%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.52 (s, 1H), 8.17 (s, 1H), 7.61 (d, 1H), 7.50 (s, 1H), 7.15 (d, 1H), 2.50 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.86, 137.72, 136.50, 132.74, 124.42, 115.46, 114.93, 77.48, 77.16, 76.84, 21.68. HR-MS (ESI) calculated for $C_8H_8N_2$ $[M+H]^+$: 133.0761, found: 133.0760.

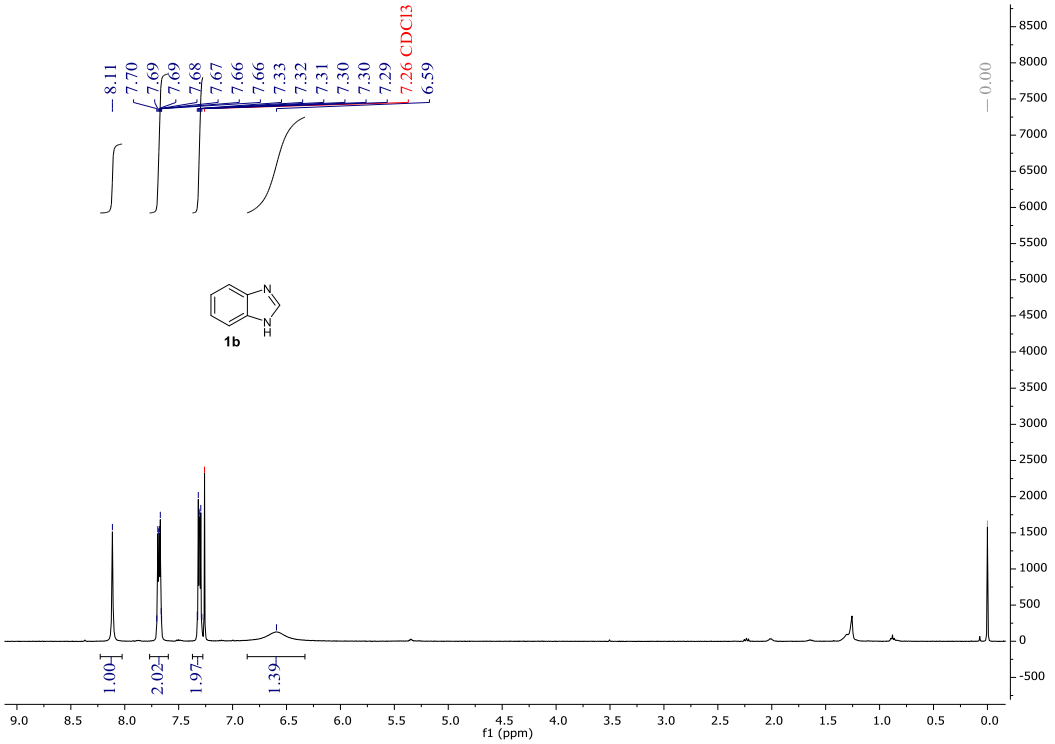
6-methoxy-1H-benzo[d]imidazole (**5b**): White solid, yield=85%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 8.06 (s, 1H), 7.56 (d, 1H), 7.11 (d, 1H), 6.94 (d, 1H), 3.83 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.51, 140.18, 137.55, 132.82, 116.33, 112.48, 97.48, 77.16, 76.84, 76.52, 55.65. HR-MS (ESI) calculated for $C_8H_8N_2O$ $[M+H]^+$: 149.0710, found: 149.0709.

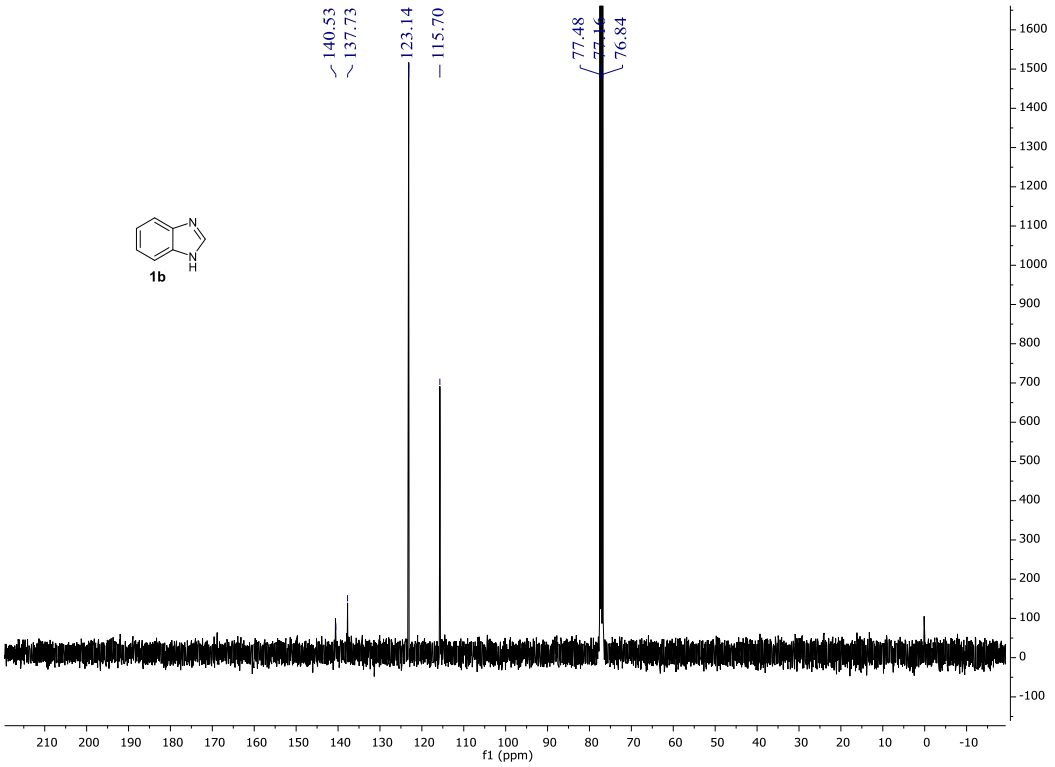
6-chloro-1H-benzo[d]imidazole (**7b**): Yellow solid, yield=86%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.79 (s, 1H), 8.24 (s, 1H), 7.66 (s, 1H), 7.58 (d, 1H), 7.26 (d, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.69, 136.62, 128.75, 123.72, 116.40, 115.47, 77.48, 77.16, 76.84. HR-MS (ESI) calculated for $C_7H_5ClN_2$ $[M+H]^+$: 153.0215, found: 153.0214.

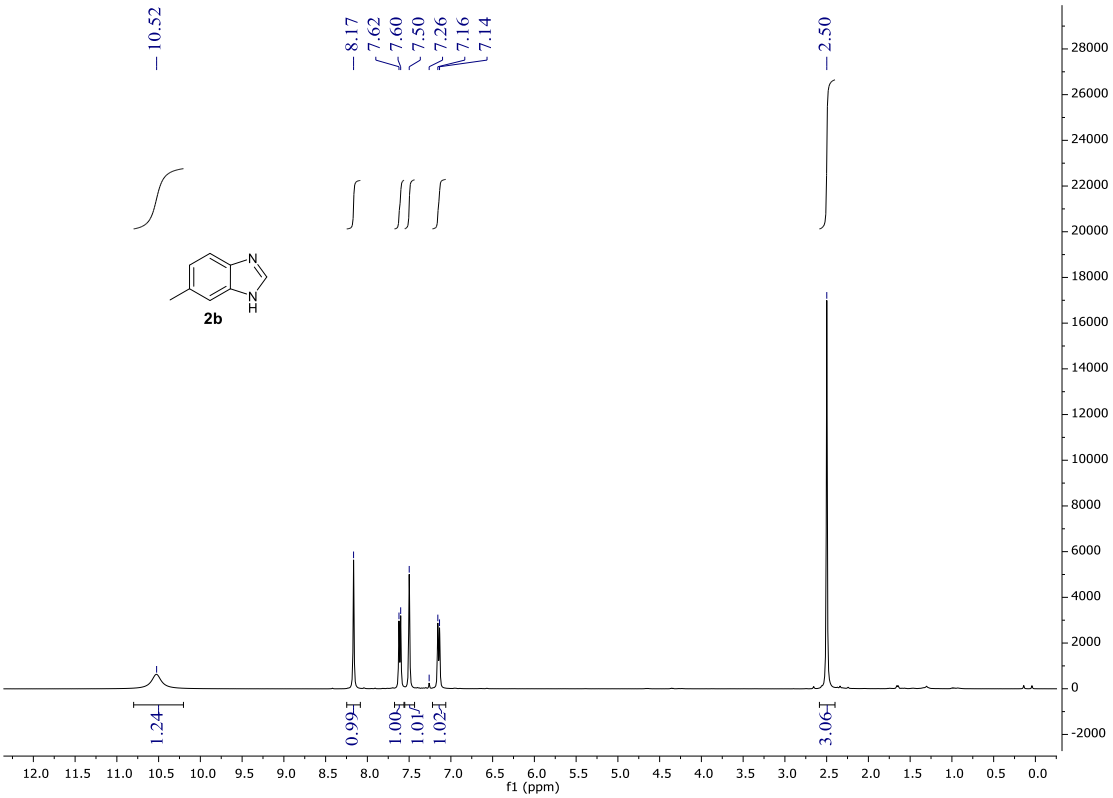
Benzothiazole (**18b**): Yellow solid, yield=92%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.13 (d, 1H), 7.92 (d, 1H), 7.49 (t, 1H), 7.41 (t, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.92, 153.24, 133.71, 126.17, 125.54, 123.63, 121.89, 77.48, 77.16, 76.84. HR-MS (ESI) calculated for C_7H_5NS $[M+H]^+$: 136.0217, found: 136.0215.

Benzoxazole (**19b**): Yellow solid, yield=70%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.78 (m, 1H), 7.60-7.50 (m, 1H), 7.42-7.30 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.57, 150.02, 140.10, 125.65, 124.64, 120.66, 111.01, 77.48, 77.16, 76.84. HR-MS (ESI) calculated for C_7H_5NO $[M+H]^+$: 120.0446, found: 120.0444.

^{1}H and ^{13}C NMR spectra of the products



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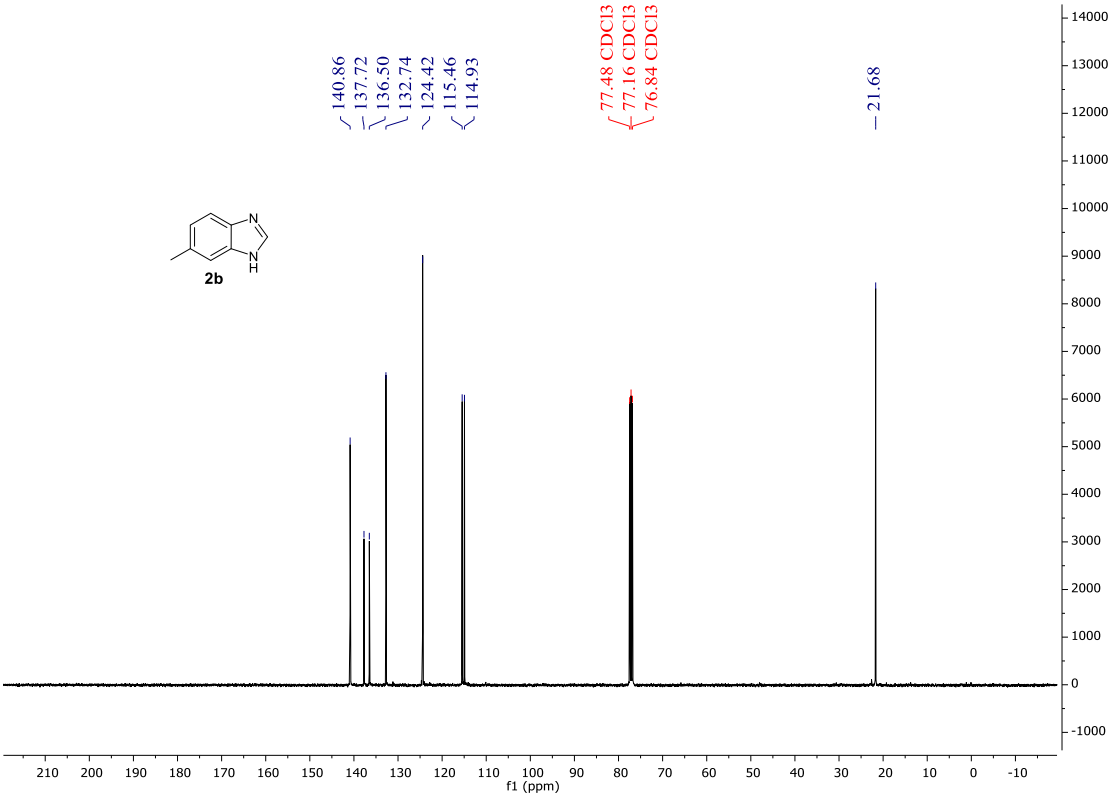
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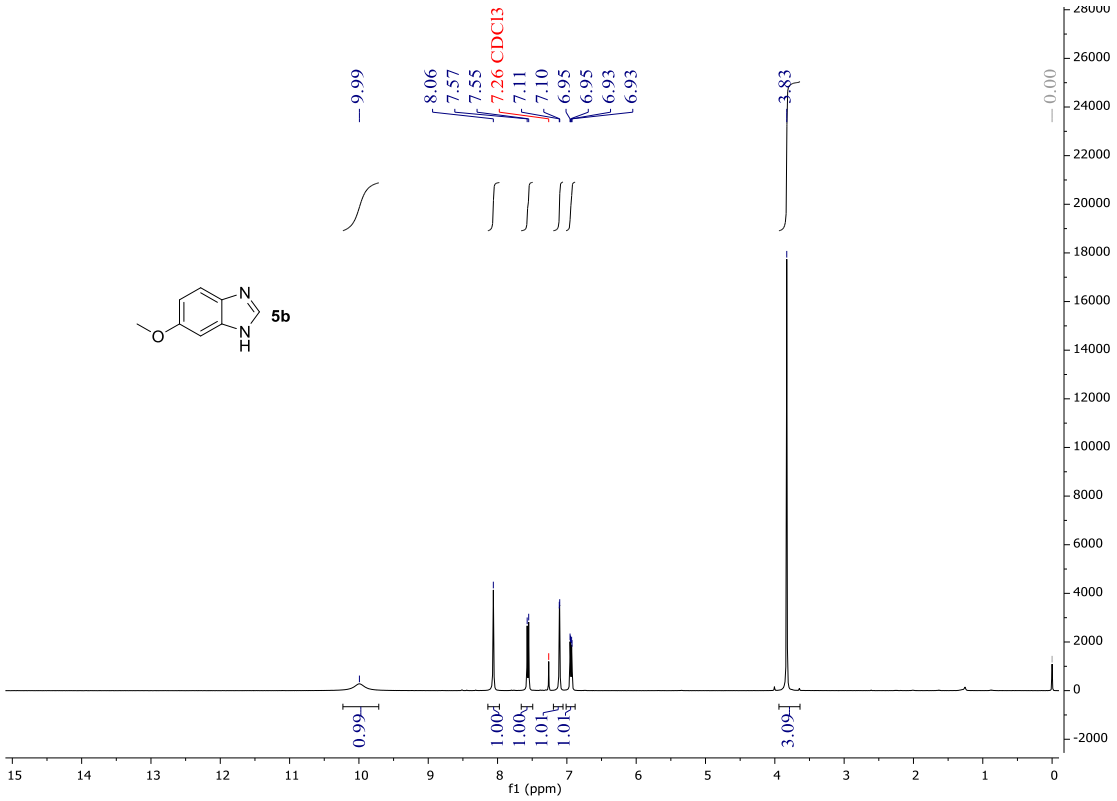
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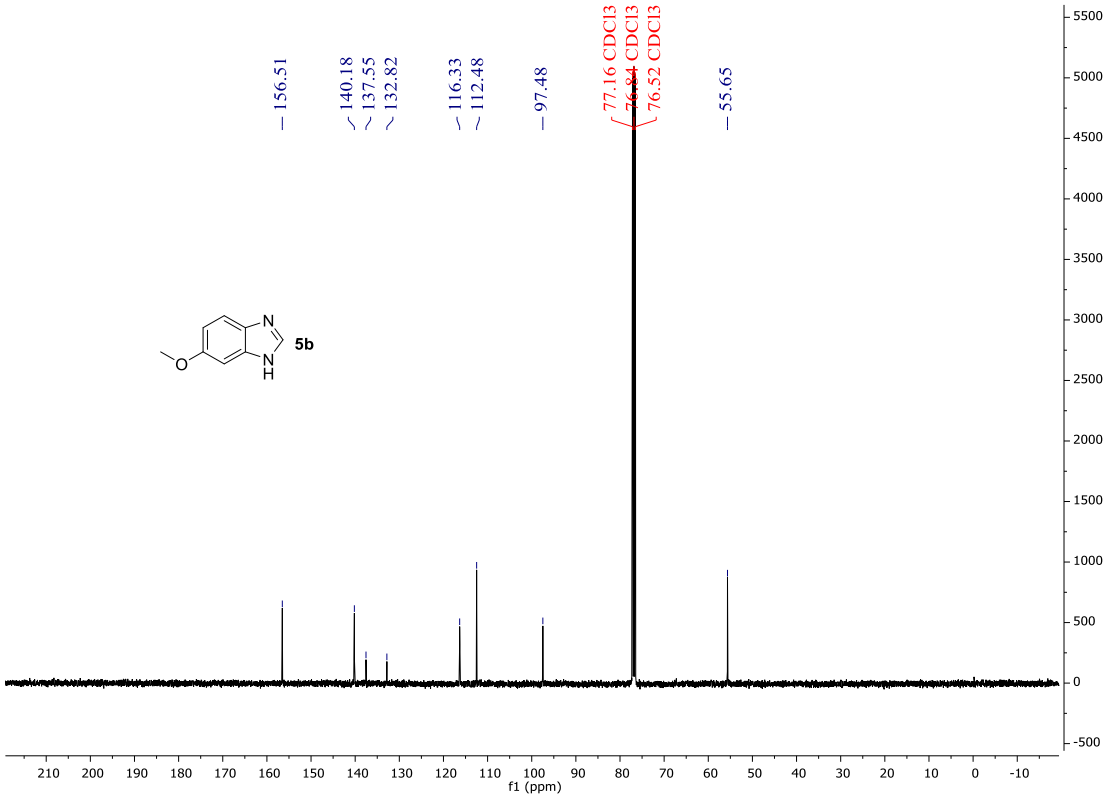
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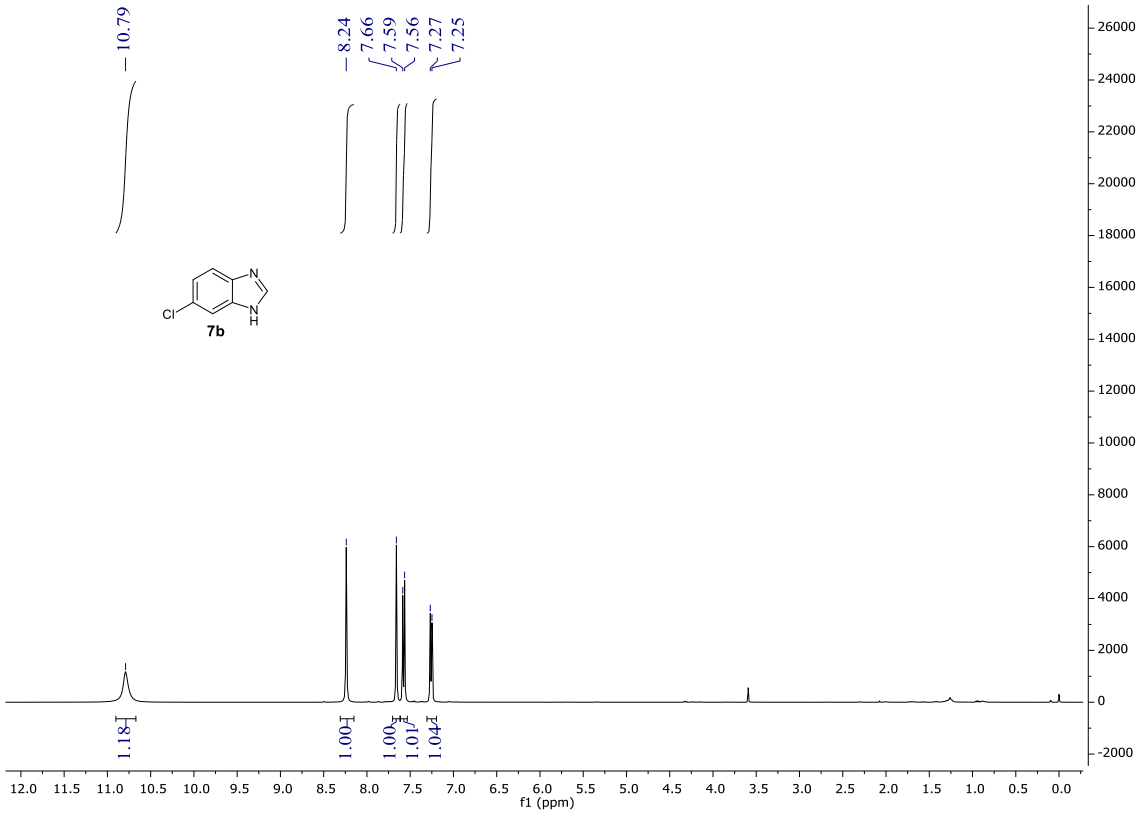
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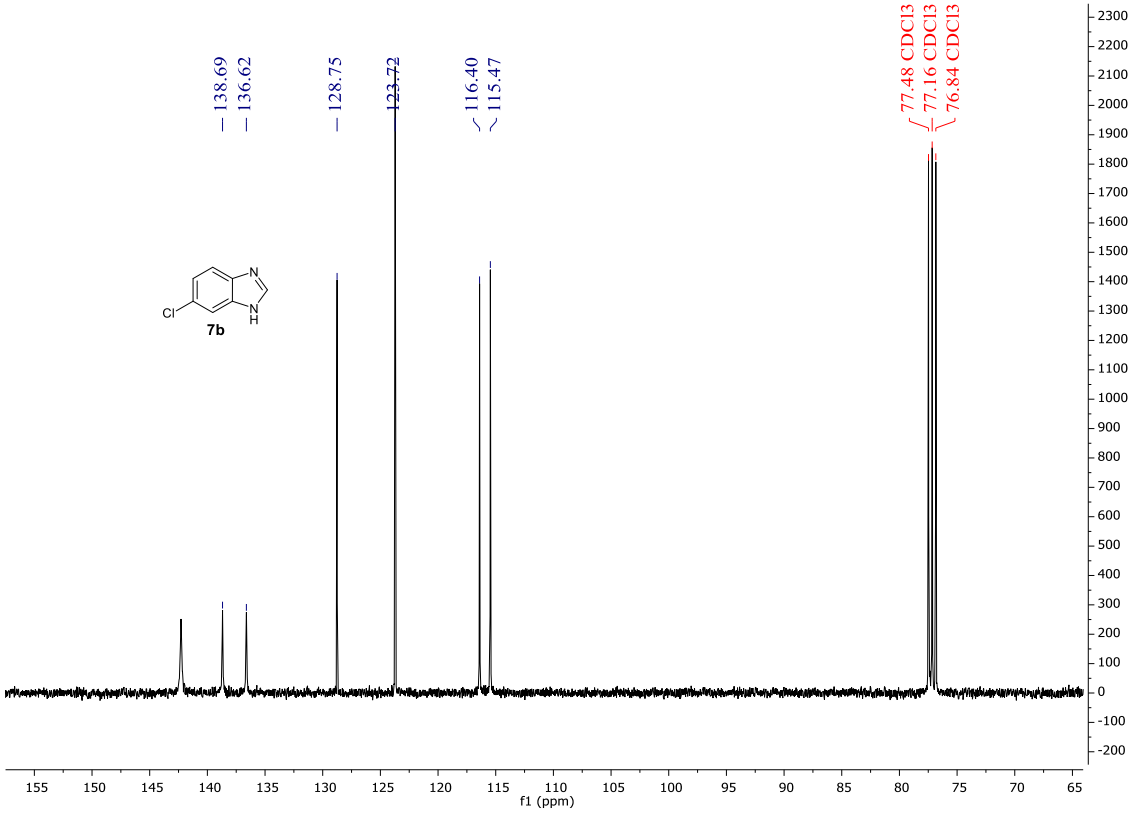
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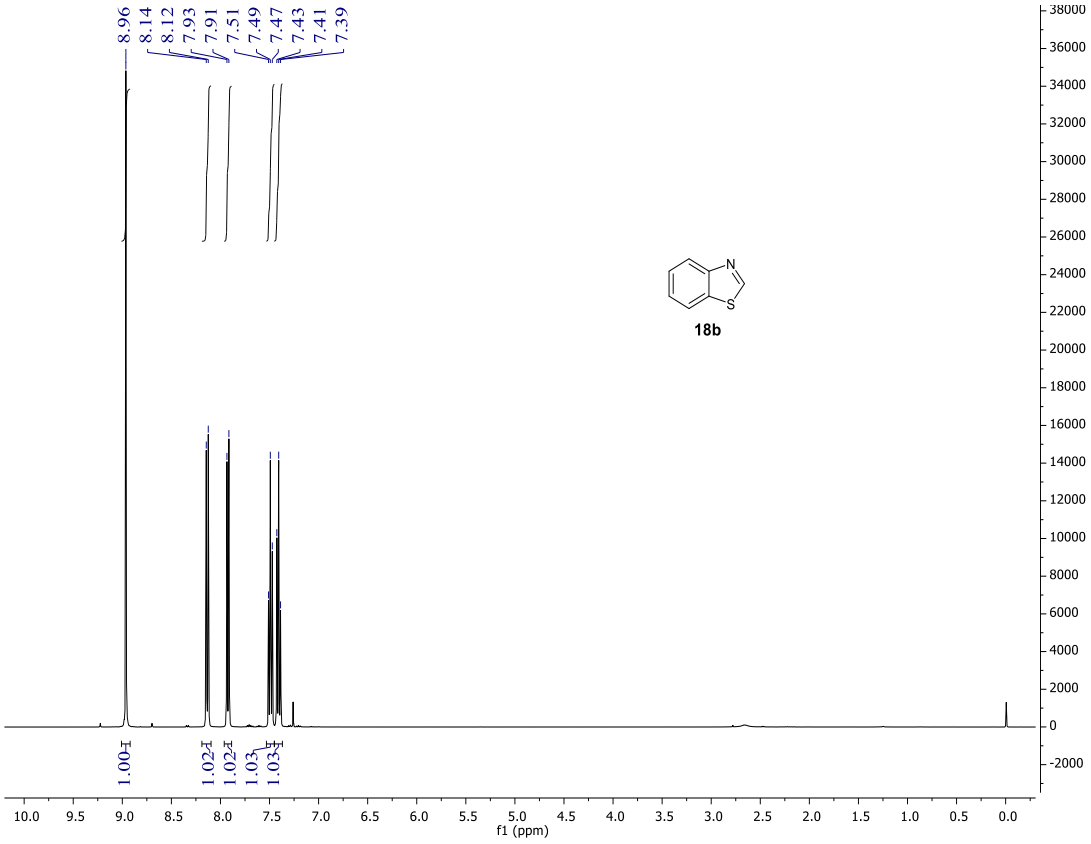
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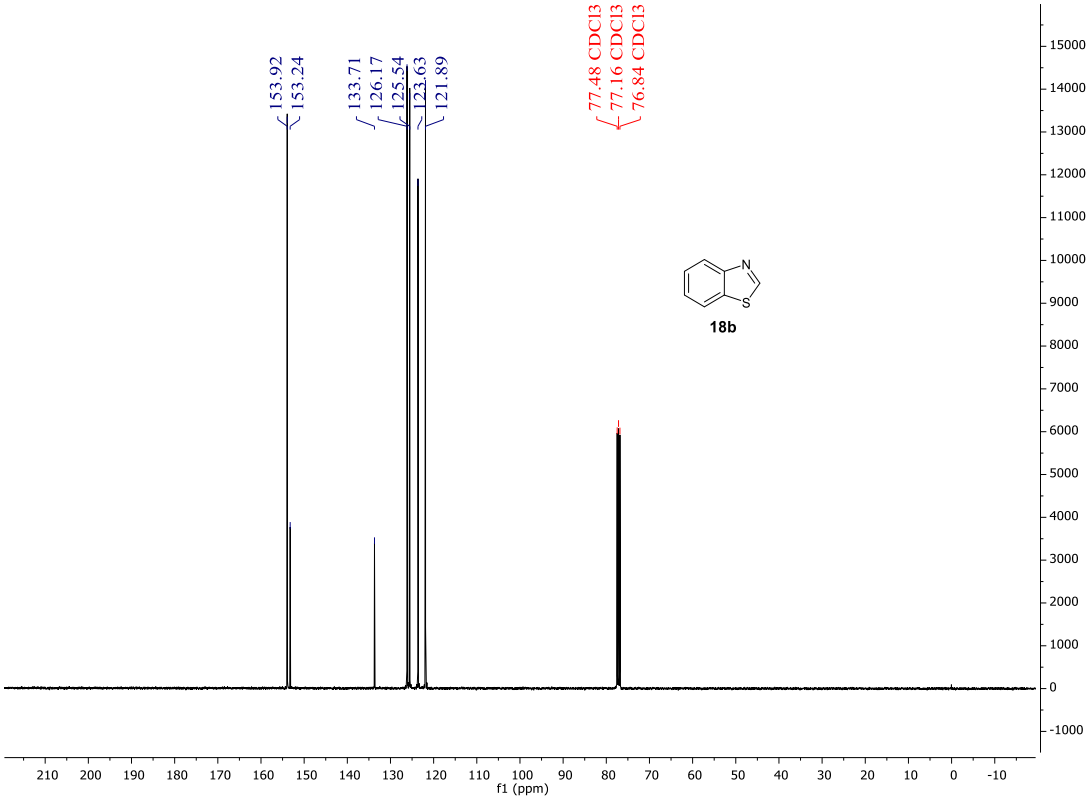
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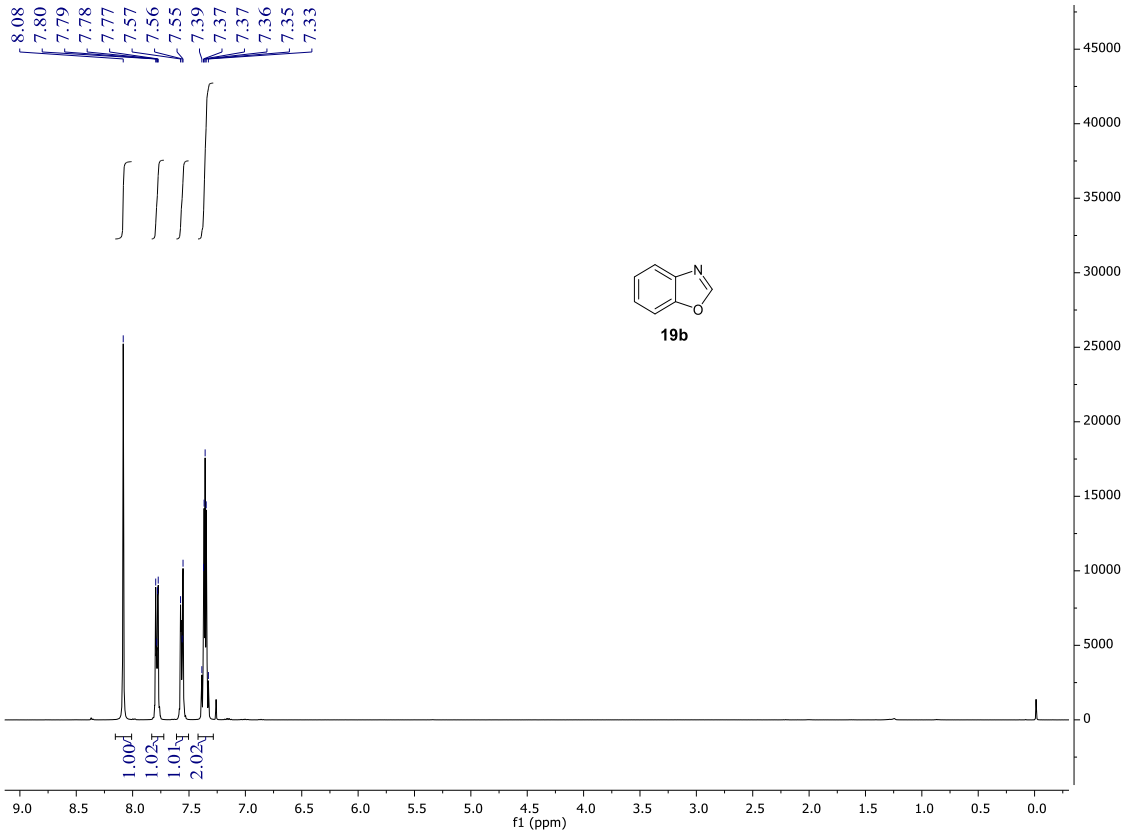
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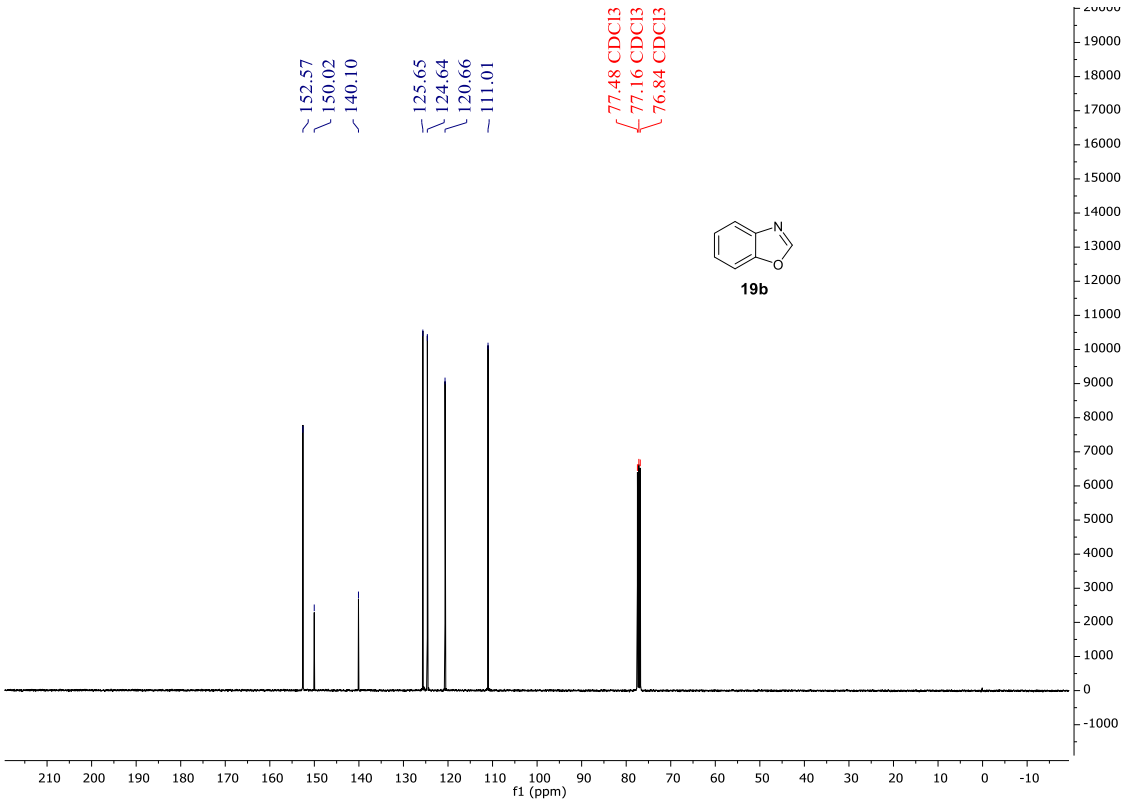
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f1 (ppm)

References

[1] Yu, B.; Zhang, H.; Zhao, Y.; Chen, S.; Xu, J.; Huang, C.; Liu, Z., Cyclization of *o*-phenylenediamines by CO_2 in the presence of H_2 for the synthesis of benzimidazoles. *Green Chem.* **2013,** *15*, 95-99.
[2] Hao, L.; Zhao, Y.; Yu, B.; Zhang, H.; Xu, H.; Liu, Z., Au catalyzed synthesis of benzimidazoles from 2-nitroanilines and CO_2/H_2. *Green Chem.* **2014,** *16*, 3039-3044.